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Integration of Sensor Technologies into Respirator Vapor Cartridges as End-of-Service-Life Indicators: Literature and Manufacturer's Review and Research Roadmap

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| 14. ABSTRACT This report provides a state-of-the-art review of sensor integration into respirator vapor cartridges for end-of-service-life indication (ESLI). The study identifies current research and available products for use as ESLI. In addition, this report provides a roadmap for research and development to the National Institute for Occupational Safety and Health (NIOSH), National Personal Protective Technology Laboratory (NPPTL). The approach was to conduct a literature survey and to have detailed discussions with commercial manufacturers, user-group representatives, and key research groups. This report contains a library of research papers, patents, reports, and other communications discussing integration of various sensor technologies into protection equipment. The survey also provides current capabilities of commercial sensors. This report provides a review of the literature, the results of the discussions conducted, a description of the state of the art of sensor technology, and concludes with recommendations for future research and development. | | | | | |
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INTEGRATION OF SENSOR TECHNOLOGIES INTO RESPIRATOR VAPOR CARTRIDGES AS END-OF-SERVICE-LIFE INDICATORS: LITERATURE AND MANUFACTURER'S REVIEW AND RESEARCH ROADMAP

BACKGROUND

Air purifying respirators protect workers from hazardous chemicals in their work environment. A wide variety of different air purifying respirators and filters are available and there are different products for different applications. This report is limited to chemical protection using masks with disposable cartridges, canisters, or filters. Table 1 lists the variety of cartridges that are available.

Table 1. Classes of Respirator Cartridges

| Cartridge | Types of Chemical | Example Applications |
|-----------|--|---|
| OV | Organic vapors with good warning properties | Degreasing, dry cleaning, agriculture, mining, petrochemical plants, etc |
| AG | Acid gases: chlorine, hydrogen chloride, sulfur dioxide, chloride dioxide, hydrogen fluoride | Electroplating, chemical processing, etching or polishing of glass, etc |
| F | Formaldehyde | Synthesis of formaldehyde resins, chelating agents and dyes, embalming, etc |
| AMMA | Ammonia/Methylamine | Manufacturing of fertilizer, textiles, paper or rubber, etc |
| MC | Multi Gas: OV + AG + F + AMMA | |
| MV | Mercury Vapor | |
| CBRN | Chemical/Biological/Radiological/Nuclear | First Responders |

Respiratory protection using respirators equipped with respirator cartridges are an effective method of protecting the worker as long as the mask is properly fit and the cartridges have not exceeded their capacity. However, it is difficult to determine when the cartridge service life has ended. Many factors affect the lifetime of the cartridge: the number and types of contaminants, their concentration levels, breathing rate of user, and environmental conditions such as relative humidity and temperature. In 1984, NIOSH published standards for certification of Active End-of-Service-Life Indicators (ESLI). The goal was to encourage their development. Until that time, little research was conducted and documented. ESLI investigations began to appear in the scientific literature in the late 1980s and early 1990s, however, most of the literature was devoted to documenting the limitations of activated carbon in varying environmental conditions and mixed contaminants.

In 1998, the Occupational Safety and Health Administration (OSHA) promulgated revised respiratory protection standards that changed the way chemical cartridges were selected and used. Under the current regulations [OSHA Standard 1910.134(d)(3)(iii)(B)(2)], either an ESLI or a change-out schedule is required to determine when a cartridge must be replaced. Formerly, users discarded cartridges when they sensed gases and vapors either by smell, taste, or irritation. Relying on users to sense

contaminant breakthrough is highly subjective. Furthermore, the concentration level for some hazards that is detectable by human sensory systems exceeds the permissible exposure limit.

The availability of end-of-service-life indicators is currently very limited, and there are no ESLIs for organic vapors. The exact number of workers that require some kind of change-out schedule or ESLI is difficult to assess. However, some anecdotal and surveillance data exists to help provide some estimate of the problem. It has been estimated that over twelve million gas/vapor respirator cartridges are sold in the United States each year. According the NIOSH/BLS <http://www.cdc.gov/niosh/docs/respsurv/> survey of respirator usage among private sector businesses in the United States, an air-purifying respirator (APR) was used in the previous twelve months at 267,467 establishments. The two most common gas/vapor substances, paint vapors and solvents, were present in 41.8% and 32.3%, of those establishments, respectively. These two classes of hazards were most commonly found (> 20%) among the construction, manufacturing, or services industrial sectors. The survey was also used to identify indicators of potentially inadequate respirator programs. One of the survey questions was on the establishments policy regarding when to replace gas/vapor filters for APRs (i.e., implement a change-out schedule). Table 2 lists the survey results as a percentage of establishments answering the question using the listed answer. Shown in the table are the general industry results (all sectors combined), followed by the construction, manufacturing, and services sectors. It is surprising that nearly 20% of the establishments allow their employees to determine when to change their gas/vapor cartridge. Workers at these establishments are at a higher risk of exposure because of potentially inadequate change-out procedures. ESLI devices could potentially reduce exposures for those workers.

Table 2. Determination of Respirator Gas/Vapor Filter Change-Out Policies (from NIOSH/BLS Survey, Respirator Usage in Private Sector Firms, 2001 adapted from Table 56, page 133-134)

| Establishment Practice | Percent of Establishments | | | |
|---------------------------------------|---------------------------|--------------|---------------|----------|
| | General Industry | Construction | Manufacturing | Services |
| Don't use gas/vapor filters | 37.5 | 43.3 | 24.2 | 43.2 |
| Respirator Manufacturer's instruction | 36.6 | 35.4 | 47.4 | 28.9 |
| Establishments own testing | 4.8 | 4.9 | 6.6 | 2.3 |
| Written change out schedule | 11.4 | 5.2 | 18.6 | 8.9 |
| Employees decide | 20.1 | 17.1 | 30.8 | 20.9 |
| Other | 6.2 | 8.2 | 8 | 1.2 |
| Don't know | 6.5 | 7.6 | 3.3 | 9.8 |

To address the need for ESLIs, the National Personal Protective Technology Laboratory (NPPTL) is interested in developing a multi-year research program to integrate various sensor technologies including MEMS-based chemical sensors into respirator cartridges to determine service life. The federal government would not manufacture these sensor devices, instead the expected outcomes of the NPPTL program may include the development and testing of prototype systems to understand the key development criteria/specifications and to support the development of NIOSH certification standards and policy documents that would encourage their use. This information would also be used by respirator cartridge manufacturers to integrate sensor technologies into their future product lines. The purpose of this roadmap is to provide guidance to NPPTL, its stakeholders, and partners on future procurements and research project needs.

OBJECTIVE

The objective of this report is to provide a state-of-the-art review of sensor integration into respirator vapor cartridges for end-of-service-life indication. The focus of the study is to identify current research and available products for use as ESLI. In addition, this report provides a roadmap for research and development to the National Institute for Occupational Safety and Health (NIOSH), National Personal Protective Technology Laboratory (NPPTL).

APPROACH

The approach was to conduct a literature survey and to have detailed discussions with commercial manufacturers, user-group representatives, and key research groups. A summary and analysis of current and future methods for the determination of service lifetimes of respirator cartridges was developed based on the review. This activity creates a library of research papers, patents, reports, and other communications discussing integration of various sensor technologies into protection equipment. The survey will also provide current capabilities of commercial sensors. Appendix A provides the literature search to date. Appendix B provides a list of all the commercial manufacturers, user-group representatives, and key research groups that were interviewed during the preparation of this report. This report provides a review of the literature, the results of the discussions conducted, a description of the state-of-the-art of sensor technology, and concludes with recommendations for future research and development.

LITERATURE SURVEY SUMMARY

Respirator Cartridge Characterization

According to OSHA, "all respirator cartridges must be equipped with ESLI or an objective basis must be established for scheduled changes." Several methods have been

developed to estimate the service life of cartridges when ESLI are not available. For instance, mathematical models have been useful in estimating the service life of cartridges when a specific cartridge is used, but fail to account for mixtures of various compounds. Laboratory tests are useful in measuring the actual breakthrough time of a specific chemical in relation to a known cartridge. Field testing is also useful when an ESLI is unavailable. Unlike laboratory tests, field tests automatically incorporate atmospheric conditions that affect a cartridge's performance. Still field tests require equipment for sampling and are labor intensive.

Several authors have described the challenges of developing a respirator cartridge change-out schedule. Moyer and Berardinelli have shown that not all permeation models are correct. Their paper demonstrates that the permeation of chlorosilanes is similar to organic compounds, rather than the hydrolysis products, hydrogen chloride (HCl) as proposed. In addition, it demonstrates the effects of relative humidity on breakthrough. This paper illustrates the need for ESLI. [Moyer, 1987] Cohen and Garrison developed a field method for evaluating the service life of organic vapor cartridges. It uses respirator carbon tubes (RCT) in a manner similar to the way industrial hygienists use charcoal tubes for workplace monitoring. Using carbon tetrachloride, the RCTs were capable of predicting the performance of respirator cartridges. However, additional work is required to demonstrate that RCTs will work with mixtures and various relative humidities. [Cohen, 1989] This prediction tool was applied to 1,6-hexamethylene diisocyanate monomer by Giardino et al. They found that the Cohen and Garrison model can be used to estimate the service life of organic vapor cartridges using adsorption capacity obtained in a laboratory setting. [Giardino, 2000] Wood and Lodewyckx improved the model for calculating organic vapor adsorption rates. This will improve service life calculations, however, the effects of humidity and temperature are not considered. [Wood and Lodewyckx, 2003] In a recent paper, Wood corrects for humidity effects. [Wood, 2004]

Yoon et al demonstrate in their paper the complexity of determining respirator cartridge service life in the presence of mixtures. The authors demonstrate that the respirator response is dependent on the precise nature and specific mixture. They propose a model requiring three parameters: rate of adsorption, capacity of the carbon bed and the effectiveness of a given compound to displace a previously adsorbed compound. Using these parameters, they were able to describe the adsorption of mixtures and calculate the breakthrough curves. [Yoon, 1996] Vahdat theoretically investigated the breakthrough of binary mixtures. He concluded that three parameters are needed: flow rate, concentration, and adsorption capacity. One compound travels faster and has shorter breakthrough times. The results of this study show that under certain conditions, changing the concentration of the compounds can cause the more strongly adsorbed component to become less strongly adsorbed and travel faster. [Vahdat, 1997] Dharmarajan et al demonstrated that hexamethylene diisocyanate (HDI) is efficiently trapped on an organic vapor respirator cartridge even when the cartridge is saturated with solvent vapors. The collection efficiency for HDI was greater than 99.6 percent for 40 hours with no evidence of desorption or migration of the HDI during storage at room temperature overnight for five nights. [Dharmarajan, 2001] In another paper, Dharmarajan et al made the same conclusions for toluene diisocyanate (TDI). However,

in this paper, the authors point out that the solvents saturate the cartridge in 6 hours and workers need to be protected from the solvents as well. The conclusion is that solvent breakthrough should be used to determine the change-out schedules. [Dharmarajan, 2003]

Tanaka et al investigated the breakthrough time for respirator cartridges using different respiratory patterns. They showed that pulsating flow results in faster breakthrough than steady state flow patterns. They also demonstrated that the flow pattern for workers is as short as those using sine and triangle patterns. [Tanaka, 1996] Linders et al have done studies to determine how pulsating flow affects the breakthrough of carbon beds. They determined that the poorer performance is mainly caused by poorer mass transfer relative to the convection transport under pulsating flow, leading to a wider mass transfer zone. They conclude that pulsating flow during breakthrough measurements is necessary. [Linders, 2003] Scahill et al have developed a new method to determine volatile organic compound breakthrough time for a sorbent. The method and representative data are given in the paper. The method significantly decreases the time required to evaluate the performance of sorbent materials. [Scahill, 2004]

Osmond and Phillips focused their research on canister designs to provide improved performance and longer service life. They used performance predicting tools to optimize canister design. Using pressure drop and chemisorption performance, the physical dimensions of the adsorbent bed were investigated for their breathing resistance and adsorption performance. Improving the cross-sectional area of the adsorbent bed was shown to be more beneficial than altering the adsorbent bed depth. [Osmond and Phillips, 2001]

An excellent overview of the procedures for developing cartridge change schedules is available.[Nelson and Janssen, 1999] This report states that there are no accepted methods for estimating the service life of cartridges used in a mixture of vapors. Vincent also outlines the data required to calculate service life. Respirator cartridge performance depend on the types of contaminants, their concentrations, environmental parameters such as relative humidity (RH), temperature and atmospheric pressure, and the worker's breathing rate. He also indicates the difficulty of handling multiple contaminants found in the workplace. [Vincent, 2001]

ESLI Investigations

The development of ESLI can eliminate premature disposals of operational respirator cartridges. Vincent describes the advantages of ESLI in a number of articles. [Vincent, 2002, Vincent, 2003] In order to develop a satisfactory cartridge, the cartridge must be subjected to the variables affecting breakthrough time and adsorption processes, including temperature, relative humidity, respiratory flow rates, concentration of contaminants, and the properties of the carbon bed. The same types of studies are required for ESLI.

Maclay et al published one of the first papers exploring ESLI for respirator cartridges. The authors used chemiresistors to monitor organic vapors. The design goal focused on developing a sensor with associated electronics and LED alarm that would add no more

than 10% to the size, weight, and cost of current respirators while notifying the user when 90% of cartridge lifetime was expended. The authors concluded that the chemiresistor appeared suitable for this application. However, more development was needed to compensate for RH effects and to improve the sensitivity. [Maclay, 1991]

Moyer et al also investigated chemiresistors as ESLI for the breakthrough detection of organic vapors. Each sensor was monitored for an increase in resistance as a function of exposure to organic vapors. Calculations using the modified wheeler equation determined the best location for the sensor within the bed. Moyer found that placement in the cartridge bed provided the sensor with a reduced RH and a clean environment. Experimental results demonstrated the need for improvements in sensor sensitivity and baseline stability. Furthermore, relative humidity, temperature, and flow rate also contributed to variation in resistance and therefore must be addressed. The sensors, however, are reusable and they stabilize quickly after an experimental run. [Moyer, 1993]

Anstice and Alder demonstrated a unique approach to detecting hydrogen cyanide (HCN). Four thermocouples and a fiber optic pH probe, sensitized to HCN were used to monitor the progress of the gas through a filter bed. A neural network was used to detect the breakthrough time. The temperature and relative humidity were not controlled. The preliminary results were encouraging. [Anstice and Alder, 1999]

Tanaka et al describes detecting organic vapors with a gas detector tube, once breakthrough had occurred. The breakthrough times for organic solvents with low boiling points were relatively short. Experimental findings suggest that a gas detector tube is an efficient means of detecting breakthrough times of organic vapors. Over a hundred gas detector tubes are commercially available and offer quantitative estimates of vapor concentration. The authors state that "the gas detector tube is much more useful and sensitive than the chemiresistor sensor for detecting the end of chemical cartridge service life". However, the cost effectiveness of gas detector tubes should be considered. Since tubes are designed for specific vapors or family of vapors, it may be necessary to have several available for testing. Also, the detector tubes do not provide continuous real time responses. [Tanaka, 2001]

Surface acoustic wave (SAW) sensors have been investigated as ESLI in a series of articles by Dominguez et al. Fluoropolyol-coated SAW sensors embedded in the filter and at the exit responded in real time as the nerve agent simulant advanced through the filter. The effects of low RH on the breakthrough times were negligible. The coated sensor did not degrade after many vapor exposures. [Dominguez, 1998] Fang et al demonstrated the detection of several organic vapors with a SAW sensor array and chemometric software. The array had the ability to identify and quantify over a wide dynamic range. [Fang, 1999] Using a three-sensor array of SAW devices, at least 16 organic vapors were identified, and quantified at low- and sub-ppm concentrations. [Park et al, 2000] Park and Zellers have used a SAW array to detect, identify, and quantify solvents and solvent mixtures as they vapors permeate through chemical protective clothing. The breakthrough times for the SAW array were comparable to responses by gas chromatography (GC). The response patterns derived from the SAW array permitted

identification of neat solvents as well as binary and ternary mixtures. [Park and Zellers, 2002] Carbowax-coated SAW sensors have also shown sensitivity to 2,4-dinitro toluene in recent studies. [Kannan et al 2004] SAW sensors have also been used for the analysis of organic vapors in exhaled breath. [Groves, 1996]

Hori et al describes the detection of organic vapor breakthrough for twelve vapors using a thick film semiconductor sensor downstream from the cartridge. GC was used to monitor the vapor concentration. The sensor results showed a decrease in sensitivity with an increase in relative humidity. Still, the sensor detected vapors before or reasonably close to the time as the GC. A new respirator was developed with the sensor placed inside a covering with the output signal connected to a portable alarm device. The alarm device was able to alert the worker when the end of its service life has been reached. Unfortunately, the sensitivity of the sensor was not the same for all organic compounds and the system required much power. [Hori, 2003]

The saturation of activated charcoal cartridges has also been detected using sensors composed of porous glass optical fibers. The sensor has the advantage of being nonselective, allowing it to detect any chemical. The sensor addressed in this paper, exhibits sensitivity to toluene in the thousands ppm range. Although the current sensitivity is not desirable for practical reasons, experiments have yielded promising results. By varying the radius of curvature or altering the fabrication process, an increase in sensitivity can be achieved. [Caron, 2004]

In addition to respirator cartridges, other types of personal protective equipment (PPE) would benefit from sensors to detect breakthrough. Vojkovic et al investigated a colorimetric method for monitoring the permeation of chemical agents through protective clothing materials. The new method for monitoring dibutyl sulphide, a mustard stimulant, is based on a reaction with sodium nitroprusside in alkaline medium. It exhibited satisfactory sensitivity with no interferences due to the technological process in the manufacturing of protective clothing materials. The indicator can be deposited directly onto the clothing and offers a low-cost detection method without the need for sophisticated instruments. [Vojkovic, 1997] Others have also investigated fluorescent dyes with varying success on fabric and paper substrates for garments. [Roehl] Duncan and Dickson tested the whole-body protection performance of chemical protective ensembles using passive adsorption dosimeters that affix directly to the skin of test participants. [Duncan and Dickson, 2003] Russell et al used n-type semiconductor sensors to measure dichloromethane inside chemical protective suits. The authors indicate that sensors are needed because protective suit performance varies with different users and their daily activity. The sensors were stable with minimal hysteresis. The calibration responses were excellent, but relative humidity affected the zero response. [Russell, 1999]

Patents

This section provides a description of the patents that are relevant to ESLI. All of these patents are applicable to the development of ESLI. All of the technologies described in the following patents will need further development and testing.

Jones and Ayes have invented a visual means for indicating when a respirator cartridge has exhausted its capacity. The indicator is a colorimetric response with the vapor or gas. In addition, a catalytic agent is provided to enhance the activation and reaction of the indicator. [US Patent 4,154,586]

Leichnitz also developed a colorimetric indicator. It is located in a container open to the gas flow at a given immersion depth into the filter material. [US Patent 4,684,380]

Stetter invented a sensor that includes a vapor sensitive medium and a means of monitoring at least one property of the medium. The medium is chosen to give a response to vapors adsorbed which is comparable to the absorbent bed. The sensor is incorporated into an alarm system within the filter cartridge. Both chemiresistor and SAW sensors are given in the examples. [US Patent 4,847,594]

Vo-Dinh invented an apparatus and detection method for the permeation of hazardous or toxic chemicals through protection clothing. The methods use a spectrochemical modification technique to detect luminescence quenching of an indicator. The indicator is exposed to the chemical permeating through the protective clothing and responds to the presence of the chemical. [US Patent 5,376,554]

Debe et al invented an ESLI sensor with alarm signals to indicate varying operating conditions. The sensor responds to a given concentration of a vapor or gas of interest, then a processing device generates a signal as a function of the concentration. Alarms can indicate predetermined threshold concentrations. The indicator can also be activated when the apparatus is working outside the predefined design parameters. [US Patent 5,666,949]

Klinger has developed a detection device for testing breakthrough of contaminants through protective clothing. Breakthrough is indicated by a colorimetric response to different contaminants. [US Patent 5,976,881]

Castor invented a gas analyzer that can be adapted for use in a respirator. The gas analyzer consists of a test chamber, an inlet for sampling, and a paramagnetic sensor of sufficient sensitivity to detect gas movement. The analyzer can be adapted for use in respirators by connecting the inlet to the inspiration line of the respirator. [US Patent 6,014,889]

Ammann et al have invented a device and process indicating filter exhaustion. The device consists of a gas concentration measuring device, a temperature measuring device, and a memory unit with several fields for storing data associated with individual filters, toxins, and environmental conditions like humidity. Preset values are selected from the memory unit, from which an evaluating circuit provides an estimate of the service life of the adsorption filter. [US Patent 6,040,777]

Hoague has invented a respirator filter having a storage device for keeping track of filter usage. A storage device located in the filter communicates with the particular filtering

system. Even if the filter is used in more than one system, the storage device can still track the filter's usage. Upon reaching the filter's predetermined end-of-service-life, the filtering system can alert the user visually, audibly, or both. [US Patent 6,186,140 B1]

Bernard et al invented an ESLI based on a porous waveguide for a respirator cartridge. The ESLI consisted of an optical waveguide connected to a light source and a detector that measures the intensity of light guided and transmitted by the optical fiber. An alarm is connected to the detector and triggers when the intensity of the light drops below a predetermined level. In use, the porous optical fiber will absorb the contaminant vapor similar to the sorbent bed in the respirator cartridge, reducing the guiding and transmission properties of the optical fiber. [US Patent 6,375,725 B1]

Curado and deMedeiros invented a rotationally adjustable respirator cartridge with a colorimetric ESLI in the sidewall. The indicator was in contact with the filter medium and is visible to the wearer through a transparent window. The wearer can rotate the cartridge so that the color-changing display is in his line of sight. [US Patent 6,497,756]

Watson et al invented a residual life indicator. The indicator provides a colorimetric response to contaminants. It consists of a solid, surface active, waterproof support medium with a concentric pattern imprinted on it. An indicator dye spot is disposed in the center of the pattern. When exposed, the dye visually moves towards the outer pattern. As the response enlarges, the user can visually determine how much life remains in the adsorbent bed. [US Patent 6,701,864]

Steinthal et al have invented non-specific sensor array detectors for portable or wearable detection devices. The detector devices are analyte general and meet low-cost and low-power requirements. The device consists of an array of polymer-composite sensors that provide audible and inaudible alarms when contaminants are detected. [US Patent App. Pub. US 2004/0135684 A1]

Gerder et al have invented a breathing gas tube for a respirator, in which a contactless interface is achieved between the signal line and the sensor. Sensor data is transmitted by one or more fiber optic waveguides at the optical interface. The fiber optic waveguide can be bonded to the gas tube, or it can be vulcanized to the tube material itself. The sensor can be designed as a single sensor or a combination for detecting and measuring temperature, humidity, gas flow, or gas concentration. [US Patent App. Pub. US 2004/0135684 A1]

DISCUSSION RESULTS

Manufacturers

In an effort to understand the ESLI needs from a manufacturers' point of view, teleconferences were conducted with Scott Health & Safety, Moldex, Survivair, Draeger and 3M. In addition, a site visit and discussion was also held at MSA. Each of these companies responded to a NPPTL federal register notice seeking partners for the development of ESLI. The links to the Federal Register Notice are:

<http://a257.g.akamaitech.net/7/257/2422/06jun20041800/edocket.access.gpo.gov/2004/04-18219.htm> and

<http://a257.g.akamaitech.net/7/257/2422/06jun20041800/edocket.access.gpo.gov/2004/04-19931.htm> Some of these manufacturers have active ESLI programs, while others do not. All the manufacturers agreed that the ideal ESLI would be an asset, but they differed in how achievable a sensor would be in the near future. The list of questions below was prepared for the discussions.

Cartridge Issues

- How does the company take into account the variables in adsorption capacity when estimating the service life of a particular respirator cartridge? (i.e. worker respiration, mixtures, concentrations, etc..)
- How do periods of nonuse, following previous chemical exposure, affect cartridge service life?
- What research has been done in altering the physical dimensions or properties of the sorbent beds to increase breakthrough time and yield a better adsorption capacity?

ESLI

- What are the issues associated with embedded ESLI?
 - How do variables such as humidity, temperature, and flow rate affect the indicator's performance?
 - What are the response times for such indicators?
- Are there any ESLI that have been considered or applied to respirators besides the already available colorimetric indicators?
- What technologies are promising for ESLI?
 - What classes of compounds can these indicators detect? And has any research been done to further the detection capabilities of current end-of-service-life indicators?
- What are the current limitations? Power? Size?
- What indicators have been developed to detect environments containing a mixture of organic vapors?

Cartridge Issues

All of the manufacturers have models available for their customers for estimating the service life of a particular respirator cartridge. They recommend that the user understand his/her work environment and err on the side of caution. The manufacturers did not expect long periods of nonuse. They expect a cartridge to be used continuously for a work shift then discarded. They do not recommend storing the cartridges following a chemical exposure. Each manufacturer believes his cartridge has been optimized for performance.

ESLI

All of the manufacturers identified many issues associated with embedded ESLI. Their biggest concerns were cost and shelf life. The total cost including sensors and electronics cannot exceed 10% of the total cost of the cartridge and mask. The sensors must cost less than \$1/cartridge and the electronics must cost no more than \$20-50/mask. The shelf life is expected to be at least 3-5 years of storage. And once the sensor is activated, it must be functional for six months to one year. The manufacturers are also concerned about repeatability, placement of the sensors, ease of use, user-interface, and effects of variables such as humidity, temperature, and flow rate. Manufacturability and power were also very important considerations. Appropriate response times were not discussed.

To date, only colorimetric indicators are commercially available as ESLI. The colorimetric indicators that are used now have limitations. They cannot be used by the color blind individuals, and the chemistries are not usually universal. They also require the user to check for color change, and do not have active alarms.

Other technologies are being considered and may be applied to respirators in the future. Some of the most promising identified are nanotubes, SAW sensors, and MEMS devices. They expect the active sensors will have microchips included to monitor variables, model the environment and compensate for variations.

The manufacturers agree that indicators are useful for users, particularly those that want to use the cartridges intermittently. The greatest need is for First Responders because they have an unknown environment, with no one telling them when to change out the cartridges. Some analytes migrate through the cartridge during storage, therefore, ESLIs would make intermittent use safer.

Other applications were also cited. The manufacturers indicated that there are niche markets that would greatly benefit from ESLIs. They thought these niche markets would be a good place to introduce the technology. Some examples were given such as inorganic chemicals that are not suitable for air-purifying respirators due to their high toxicity and lack of smell, taste, or irritation at safe levels. These chemicals require atmosphere-supplying respirators, which are much more expensive to use and are more uncomfortable for the workers to wear. An appropriate ESLI may make some of these chemicals acceptable for air-purifying respirators and therefore greatly reduce the cost of protecting the workers. ESLI are also needed for organic vapor cartridges. In particular, ESLIs are needed for complex work environments where mixed analytes are present and

difficult to model. Volatile solvents are a big concern because the chemicals are frequently present at elevated concentrations and they are known to travel quickly through the filters. ESLI for mixed organic environments are expected to have a large market and target many of the workers that need the technology.

Some manufacturers have active research programs to advance the detection capabilities of current end-of-service-life indicators. However, some companies believe the market will not be willing to pay the additional costs for ESLI. They believe, regulations will be necessary to drive the development of ESLI. They also indicate that cleaning the masks could be an issue with active sensors and the associated electronics. Shock, vibration, and EMI shielding will also be important considerations given the workplace conditions in which some masks are used.

The current limitations to the development of ESLI are power, size, weight, reliability, ruggedness, and the lack of cost effective technologies. Some manufacturers are gaining experience, investigating promising results, but are not ready to manufacture embedded sensors. They identified many issues. Communication from sensor to user was one concern. Transfer problems are also a concern. Ideally, the sensor would be placed in the center of the filter bed. To avoid transport problems within the cartridge, they expect the sensors to be comparable in size to the carbon particles. However, preliminary results with embedded sensors have shown that for properly designed cartridges, the wave front of the vapor or gases is uniform and predictable, so sidewall sensors may be suitable. More work is needed to fully assess sensor placement and performance. The manufacturers point out that any sensor embedded in a cartridge would be expected to function in any work environment and the user would expect a certain level of performance. One manufacturer said that the regulations need to be clarified because manufacturers are not clear on the specifications for the sensors. Performance characteristics must be defined.

The ESLIs that are currently available are limited. North Safety Products uses a colorimetric strip to indicate ESLI for a few compounds: TDI, HCl, hydrogen fluoride (HF), sulfur dioxide (SO₂), and hydrogen sulfide (H₂S). For remaining vapors, North indicates that a change schedule should be implemented. 3M has a respirator equipped with an ESLI when working with mercury vapor. MSA has a cartridge life expectancy calculator on their website and respirators that have an ESLI suitable for mercury vapor.

The ideal sensor would be a universal detection with very low cost and extremely small size. It would have a wide range of selectivity with sensitivity in the appropriate concentration ranges for all chemicals. It would be robust and not require calibration. The sensor would be able to sit dormant for years with no degradation, then work flawlessly for any period of time the user requires. All of the manufacturers indicated that they were willing to assist in any development efforts with NIOSH. They said they could prototype cartridges with embedded sensors.

User Groups

The user groups indicated that ESLI were highly desirable among the workers. Employers frequently do a bad job of implementing respiratory protection programs. The decision to change cartridges is left up to the wearer. An ESLI would benefit the user, and would allow them to be less dependent on the employer programs. The users would like simple user interfaces with an active warning to the wearer. Workers are willing to pilot new technology and would be available to provide feedback to developers. Young workers are becoming very comfortable with technology and will accept new methods. Durability is very important to the users.

Research Groups

NPPTL Respirator Cartridge End of Service Life Indicator Program

The National Personal Protective Technology Laboratory (NPPTL) has the responsibility to prevent work-related illness and injury by ensuring the development, certification, deployment and use of personal protective equipment and fully-integrated, intelligent ensembles. Their four main focus areas for scientific research are (1) respiratory protection, (2) sensors and technology development, (3) human performance, and (4) fully integrated, intelligent ensembles. The topic of this report is respiratory protection and sensor and technology development. In this research area, NPPTL has three ongoing projects, end-of-service-life modeling, developing and integrating chemical sensors for real-time determination of respirator cartridge service life, and colorimetric indicators for breakthrough detection in protective clothing.

NPPTL has been very active in the end-of-service-life modeling. [Wood, 2004] <http://www.cdc.gov/niosh/updates/upd-12-22-03.html> In collaboration with Los Alamos National Laboratory, a single vapor model that corrects for relative humidity effects was developed and incorporated into a user-friendly software program. The model and computer software have been well received by government and industry. In collaboration with its stakeholders and research partners, NPPTL is currently developing an estimator for reactive gas cartridges. In addition, they are working on a multiple organic vapors model that includes relative humidity effects. The multiple organic model is complex and includes competition among vapors, displacement of vapors and water, as well as adsorption kinetics. Eventually, all the models will be combined into one widely available calculator/estimator.

NPPTL has also been actively involved in the development of ESLIs. The goal is to develop a respirator with embedded sensors for active indication of cartridge exposure as shown in Figure 1. They have conducted preliminary studies using Cyran Sciences (now Smiths Detection) sensors. A typical 32 sensor array was modified to include 8 conductive polymer composite sensor elements on a flexible printed circuit as shown in Figure 2. The sensor array has been embedded into a filter cartridge for volatile organic vapors, see Figure 3. A prototype is ready for integration and testing.

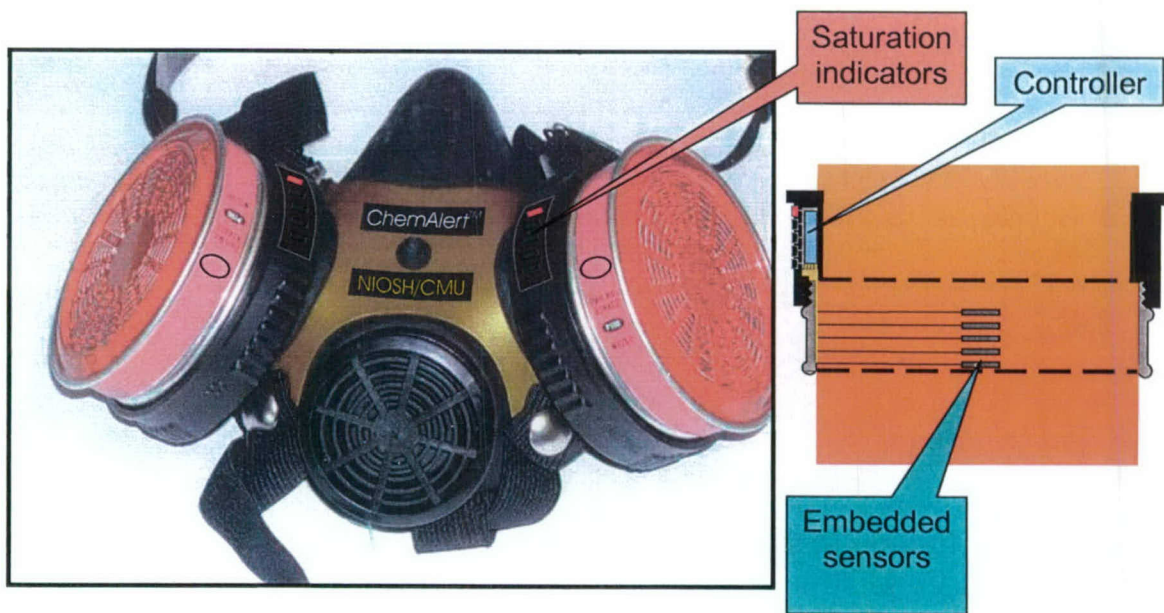


Figure 1. Diagram of conceptual respirator with filters that include saturation indicators, controller, and embedded sensors.

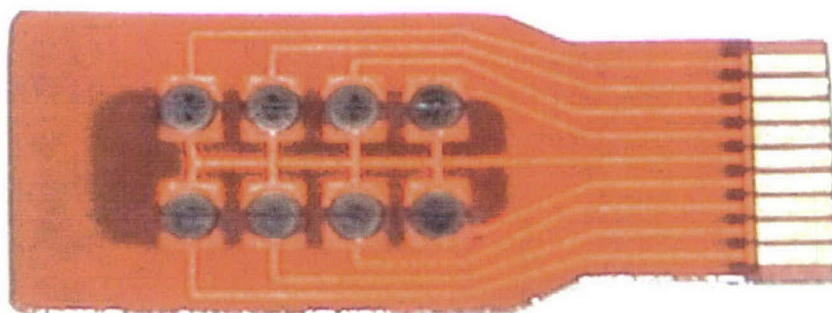


Figure 2. Flexible printed circuit with eight conductive polymer composite sensor elements.

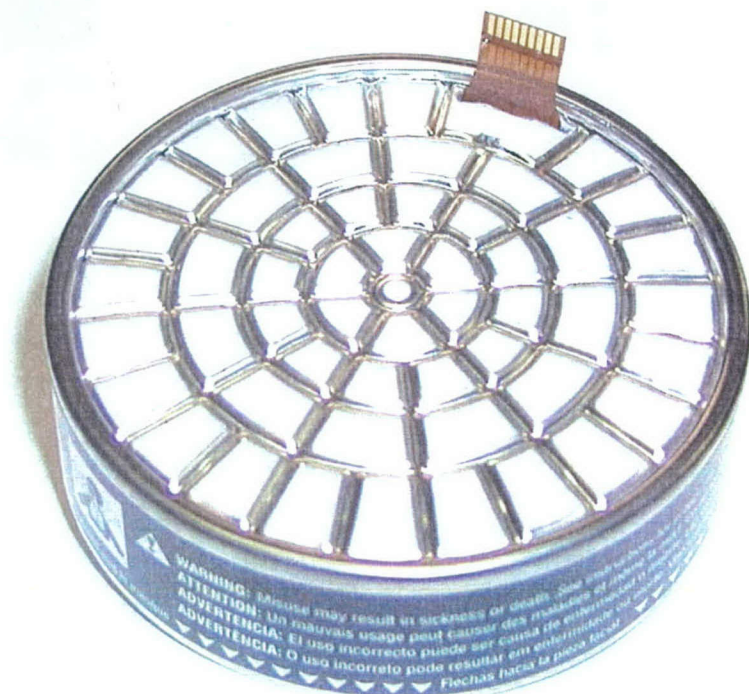


Figure 3. The sensor array embedded into a filter cartridge.

In addition, NPPTL has an ongoing research program with Carnegie Mellon University to develop low cost, multi-modality sensors. The chemical sensors are being developed using chemically sensitive nanostructured polymers with complimentary metal-oxide semiconductor (CMOS) technologies and microelectromechanical systems (MEMS). A variety of semiconductive regioregular polythiophenes-based polymers and block copolymers have been synthesized. Novel coating methods are being explored. The sensors have been designed to detect conductivity, gravimetric, and stress changes in the polymers in response to gas analyte exposure. [Fedder, 2004]

In response to a Federal Register Notice ,

<http://a257.g.akamaitech.net/7/257/2422/06jun20041800/edocket.access.gpo.gov/2004/04-19931.htm>, cartridge manufacturers have indicated a willingness to collaborate in studies to incorporate sensors in the cartridge beds. These studies are expected to investigate sensor performance during test loading of cartridges with industrial solvent vapors.

Joint Services General Purpose Mask (JSGPM)

The US military has adopted a new general purpose mask with a moisture indicator. The moisture sensor is colorimetric and it is inside the cartridge with a viewing window to see the color change. The moisture sensor is intended to alert the wearer that the filter has degraded due to excessive exposure to air. The joint services are happy with this level of

ESLI because it is a simple, low cost solution that requires no power, is easily supportable in the field, and does not add additional weight to the mask.

The moisture indicator is not the technology that the military had hoped to use, but it is also a huge improvement over current methods. In determining the best ESLI for the new joint services mask, a review of the available technology was conducted. In the end, they concluded that there are too many unknowns for a specific detector other than moisture to be selected due to the unique mission of the warfighter. No universal indicators are currently available for the variety of chemicals that may be encountered. In addition, the warfighter must travel light, he is on the move, and does not have access to an extensive supply train. Unlike most domestic applications, where the workers are in a known environment for up to 8 hours/day, the warfighter may or may not be exposed and he is uncertain of the parameters in his working environment. In many ways his situation is similar to the first responder, but he does not have the advantage of a supply system to provide needed parts and maintenance.

The military feel that this technology is the best for the way a mask is typically used by the warfighter. The typical use is outlined below. The mask is issued to a warfighter. He opens the cartridge and installs it when he expects a chemical exposure. The exposure may not occur. The cartridge is not discarded until it has been exposed to hazardous chemicals or has been degraded by over exposure to air. The moisture sensor is the first indicator of actual exposure to air. Previously, the time was estimated.

US Army Residual Life Indicator Research Program

The US Military has had a research program investigating residual life indicators for 20 years. Due to the unique working environment of the warfighter, the ideal sensor is a universal sensor for all chemical contaminants of interest with extremely low power requirements. The military is concerned with protecting the service man and woman from chemical agents, smoke, obscurants, burning substances, fuels, and toxic industrial chemicals. After conducting feasibility studies on several technologies and methods, scientists at the Edgewood Chemical and Biological Center (ECBC) dropped plans for developing a universal detector and instead, focused on specific chemicals. The chemicals of interest are both organic and inorganic.

In an effort to determine the best technologies for ESLI, the US Army sponsored a workshop in October 2002 and invited representatives from industry, universities, and government researcher to participate. About 50-70 participants attended the workshop. In addition, a technology survey was conducted in 2000. [Lawhon, 2000] The report reviews the state-of-the-art of several technologies considered for ESLI. However, the main focus of the report was colorimetric methods that could be used with no power requirements.

The US Army researchers have investigated both active and passive detectors; however they do not believe that most active sensors are mature enough to be used as ESLI in masks in the near future due to the extreme conditions placed on the sensors for military use. The logistical issues alone eliminate many of the promising technologies. The

principal investigator, Mr. Gardner, a research engineer at ECBC, considers the road blocks for development of active sensors are (1) sensitivity, (2) environmental stability, (3) size, (4) insufficient database on sensor responses to military target agents, (5) interferences, (6) vast operational conditions, (cannot satisfy all the requirements for all uses), and (7) shelf life. However, they continue to monitor the progress in sensor development and still desire an active sensor.

Colorimetric technology is the primary focus of their current research. The indicator film is placed along the perimeter of the sorbent bed where it will react with contaminants as the wave front of the chemicals advance through the filter bed. The indicator can be viewed through a transparent window in the filter housing. The indicator was chosen because of its ease of use, cost, size and sensitivity. Candidate indicator films were evaluated for sensitivity to different target gases. The more promising candidates are those designed to detect acidic agents or acidic degradation byproducts. Though one ESLI film is not suitable to detect all target agents, a combination of multiple indicators should be sufficient in detecting the majority of agents. [Gardner, 2001]

Chemical Sensor Technologies for Air Filter Lifetime

Dr. R. Andrew McGill at the Naval Research Laboratory has been investigating the use of sensor technologies as residual life indicators for air filter beds for about 8 years. Many technologies have been investigated and several are promising for collective protection applications. Several proceedings have shown good results for SAW, chemiresistor, and photoionization detectors. [McGill, 2001 and Gardner, 2001] Several technologies are suitable for the large air filters for shipboard, vehicle, and land based collective protection because size and power are less of a concern. The goal has been to develop an interface for any available sensor technologies.

Dr. McGill also has an active research program for novel sensors. His recent research has focused on nanotubes and microcantilevers. [Pinnaduwa, 2004] These sensors have demonstrated much promise and have the advantage of being small with extremely low power requirements. These sensors are not ready for use as ESLI. Research on nanotubes is still at the basic and exploratory stage. Microcantilevers have similar humidity effects as SAW and chemiresistor sensors.

COMMERCIALLY-AVAILABLE SENSORS

Several different types of sensors are commercially available as shown in Table 3. The information in the table was collected by searching the internet and reviewing the literature. Promising sensor technologies for ESLI include SAW, chemiresistors, metal oxide sensor (MOS), optical IR sensors, nanotube sensors, electrochemical sensors, and MEMS sensors, which include microcantilevers. Even within these generic names there are many variations in sensor design. For example, chemiresistor sensors include polymers doped with carbon black, semiconductor coatings, and nanocluster metal-insulator-metal ensembles (MIME). All of these vary in performance and have shown promise as ESLI.

Table 3. Commercially-Available Sensors

| Fiber Optics | |
|------------------------|---|
| Maturity | Research involving fiber optics as ESLI has been performed |
| Sensitivity | Exhibits sensitivity in thousands ppm range for toluene. Experiments yield promising results for sensitivity improvement. |
| Selectivity | Nonselective |
| size | Relatively small |
| Special Considerations | Requires light source and necessary power. Newest sensor application ESLI technology. |
| Manufacturers | Ion Optics |
| | |
| SAW Sensors | |
| Maturity | Commercially available and incorporated in several portable detection systems |
| Sensitivity | High sensitivity in ppb range |
| Selectivity | Can detect a large range of organic vapors. Response patterns allow for the identification of neat solvents and mixtures. |
| Size | Small |
| Special Considerations | Can identify and quantify over a wide dynamic range. |
| Manufacturers | Microsensor Systems, Inc.; BAE Systems |
| | |
| Chemiresistors | |
| Maturity | Commerically available |
| Sensitivity | Sensitivity in ppm range, with potential research yielding ppb ranges |
| Selectivity | Can discriminate a variety of chemicals |
| Size | small |
| Special Considerations | Low power consumption. Automatic indication with LED Alarm. Quick stabilization after sample run. |
| Manufacturers | Microsensor Systems, Inc.; Cyrano Sciences (Smiths Detection) |
| | |

Table 3. Continued.

| Colorimetric Detection | |
|--|---|
| Maturity | Commercially available in some masks. Working towards colorimetric indicators for nuclear/biological/chemical mask filters. |
| Sensitivity | Satisfactory to good sensitivity, (ppb-ppm). |
| Selectivity | Selective for specific and class of compounds |
| Size | Sufficient size for comfort and use |
| Special Considerations | No power source necessary. Low cost. |
| Manufacturers | North, 3M |
| | |
| Metal Oxide Semiconductor Sensors | |
| Maturity | Commercially available in portable detection systems |
| Sensitivity | Limited (ppm) |
| Selectivity | Selectivity limited |
| Size | Small |
| Special Considerations | Wide temperature range with thin film metal oxide semiconductor. Relatively inexpensive. Sensitivity to humidity |
| Manufacturers | Figaro, Mircosensor Systems, Inc.; Kamina |
| | |
| MEMS | |
| Maturity | Commercially available sensors. Some interesting research report. |
| Sensitivity | Laboratory studies indicate ppb-ppm |
| Selectivity | Adsorption coating, Several modes for measurable signals |
| Size | Extremely small |
| Special Considerations | Several detection methods possible. Can be used for both chemical and biological detection. |
| Manufacturers | Protiveris |
| | |
| Carbon Nanotubes | |
| Maturity | Several companies are focused on nanotechnology applications |
| Sensitivity | Sub-ppb and ppm range |
| Selectivity | High selectivity is achievable |
| Size | Compact |
| Special Considerations | Manufacturability of commercial sensors |
| Manufacturers | Integrated Nanosystems, Inc. (INI); Nanosys Inc. |

STATE-OF-THE-ART SENSOR TECHNOLOGY

This section describes some recent developments in sensor technology that are relevant to ESLI. In some cases, sensors that have been around for many years have seen some innovative changes. In addition, novel signal processing and sensor architectures are improving sensor array performance. New concepts in smart fabrics are also being explored. Most of the work however is centered around nanotechnology. The nanotech research is provided in a section called **“Nanotech-Enabled Sensors and Sensor Systems.”**

Park and Akbar provide a detailed discussion of ceramics for chemical sensing. Ceramic oxides are attractive as chemical sensors due to their low cost and wide range of applications. Ceramic oxide-based sensors are expected to become an important sensing medium in the future due to the development of new materials, improvements in sensor fabrication and manufacturing techniques, and the application of signal processing methods. The success of sensors is also expected since efforts are focused on specific applications. [Park and Akbar, 2003] Comini et al has shown improved sensor performance of metal oxide sensors by changing the fabrication methods. They were able to make single-crystalline tin oxide nanobelts. Nanobelts have a rectangular cross section in a ribbon-like morphology. They are very promising for sensors due to the surface-to-volume ratio. [Comini, 2002]

Wilson provides interesting methods for optimizing gas sensor array for single analyte and multiple interferent applications. She concludes that small arrays are best. The resolving power of a sensor array will decrease with an increasing number of sensors. [Wilson, 2002] Wilson and Roppel have demonstrated hardware architectures to enhance the performance of chemical sensors. Homogeneous array are used to compensate for sensor variations, drift, humidity, and other environmental effects, while heterogeneous arrays are used to improve discrimination capacity. Aggregation methods use the relationships among sensor outputs to generate a different set of outputs that provide more robust concentration and discrimination information. [Wilson and Roppel, 1999]

The functionality of clothing is being revolutionized. Research is underway to develop advanced fabrics that will better protect the wearer. Included in this research are new developments in chemical and biological protection fabrics. Fabric-based sensors that can detect, respond, and decontaminate are being investigated. [Schreuder-Gibson and Realff, 2003] The U.S. Army has an ongoing project called Future Force Warrior (FFW) <http://www.natick.army.mil/soldier/WSIT/>. One of the most important goals of the project is to create strong, flexible body armor. By recreating the polymer structure of spider silk and insect exoskeletons, researchers hope to develop armor that is both flexible and durable with possible added ballistic protection. In addition to durable, lightweight, and flexible armor, the future warrior uniform will be equipped with chemical and biological sensors for detecting both harmful chemical and biological warfare agents. Some researches have proposed creating “responsive nanopores” in the uniform that will close when they detect a biological agent. [Roncone, 2004]

Nanotech-Enabled Sensors and Sensor Systems

The introduction and incorporation of nanomaterials and nanotechnology offers the potential for revolutionary transformations in the capabilities of sensors and sensor systems. Nanoscale sensor technologies rely on the unique physical and chemical properties conferred by their size. Intelligent use of such materials will permit the design of light, compact, low power, and exquisitely sensitive devices. Even old detection methods are being enhanced with the use of nanoscale materials. New sensor designs will exploit the inherent, often unique chemical and physical properties of nanoscale materials, such as engineered band structures, electrical conduction, mechanical resonance, quantum effects, optical properties, large surface to volume ratio, and small mass. For example, the large surface to volume ratio of nanoparticles translates into large changes in the electrical conductivity or mechanical resonance of the nanostructure when very small quantities of analyte adsorb on its surface. The ability to manipulate the size of the particles, and especially their surface chemistry, therefore makes them amenable to designed modifications and optimization for particular analytical tasks. These qualities also make sensors based on nanotechnology especially well suited for arrays with different chemistries and transduction mechanisms, thus enhancing their selectivity and ability to discriminate analytes in complex chemical environments. These characteristics suggest that sensors will be increasingly flexible and customizable to specific tasks as research provides suites of suitable chemistries and designs built upon common architectures. Such a sensor can be based on varying numbers of these structures, from a single particle, such as a carbon nanotube, to an amalgamation of many particles, e.g. metal beads coated with an organic layer to form a 2-dimensional layer. Other sensors rely less on the specific size-dependent properties, but still benefit from using nanoscale particles optimized for other desirable device properties, e.g. low power consumption.

Unique sensor materials are being developed that result in small and inexpensive sensors with novel sampling mechanisms. Both optical and electronic-based nanocrystal sensors are being investigated because these novel materials offer unusual and useful properties. Likewise, carbon nanotubes possess an extraordinary range of electronic, thermal, and structural properties. These properties depend on the detailed physical and chemical structure of the tube, so small changes can dramatically affect them and offer a number of possible detection pathways.

Nanotechnology is enabling sensitive new devices. Micromachined cantilevers-based sensors have a significant advantage in the absolute sensitivity achievable. Novel coating methods are making these sensors more robust and reproducible. This field is expected to advance quickly and produce some unique methods for detecting many chemical and biological species of interest.

Recent Sensor Articles

By controlling the meso-porous and nano-porous structure of the sensing material, the sensing properties of semiconducting gas sensors could be improved. In addition, the fabrication conditions of the “nanostructured semiconducting oxides” can be altered to improve gas-sensing capabilities. [Shimizu, 2004]

A single neuron sensor has been developed that provides signature patterns for a variety of chemical agents. When the chemical agents bind to specific receptors, changes in the "extracellular membrane potential" are translated into signature patterns that are unique to each agent. In addition, chemical agents studied in cascaded states can also be accurately identified. Cascaded sensing improves the possibility of single neuron sensors being applied to real time situations. In addition, the signature patterns generated under cascading conditions close to detection limits indicate the ability of the sensors to recover and their possibility for reuse. The sensor provides fast response times and a sensitivity level down to "femto-molar concentrations." [Prasad, 2004]

Snow et al have developed a new sensor technology based on nanocluster metal-insulator-metal ensembles (MIME). The sensors consist of nanometer-size gold particles encapsulated by a monomolecular layer of alkanethiol surfactant deposited as a thin film on an interdigital microelectrode. The sensor operates by absorbing vapors into the organic monolayer, which causes a large modulation in the electrical conductivity of the film. The tunneling current through the monolayer between the gold particles is extremely sensitive to very small amounts of swelling and dielectric alteration caused by the absorption of the vapor. Selectivity is achieved by varying the chemical functionalities at the terminal structure of the alkanethiol surfactant or substitution of the entire alkane structure. [Snow, 2002] A table provided by Dr. Snow comparing MIME sensors to other types of sensors is given in Appendix C.

Zellers et al has recently investigated wireless microanalytical systems for homeland security applications. The microsystem incorporates micromachining (MEMS) technology to fabricate chromatographic separation channels. Several sensor technologies are being considered including chemiresistor arrays with gold (AU)-thiolate nanoclusters. These new sensors look very promising and have demonstrated detection limits two orders of magnitude lower than those achieved with SAW sensors. [Zellers, 2002]

A chemical vapor detection and biosensor array based on miniature flexural plate wave (FPW) devices has been fabricated. FPW devices can function in vapor or liquid gels and have higher sensitivities at lower operating frequencies than other comparable devices. Through micro-chemical analysis arrays using FPW sensors, vapor phase nerve agents and infectious biological agents can be detected. Detection is achieved by monitoring changes in the frequency and damping of the resonance during environmental interaction. [Cunningham, 2001]

In May 2002, A Grand Challenge Workshop Series was conducted called "Nanotechnology Innovation for Chemical, Biological, Radiological, and Explosive Detection and Protection." The report says that nanotechnology offers the potential for orders of magnitude improvements in sensitivity, selectivity, response time, and affordability. In the report, microcantilevers are identified as sensors with extremely high sensitivity, selectivity, and wide dynamic range. Nanostructured films are also identified as materials with promising sensing characteristics. [Nanotechnology-Workshop Report, 2002]

Carbon nanotubes have recently been used for chemical sensors. Li et al fabricated a gas sensor by simple casting of single-wall carbon nanotubes on an interdigitated electrode. The sensor responses were linear for concentrations of sub ppm to hundreds of ppm with detection limits in the ppb range for nitrogen dioxide and nitrotoluene. The response occurs within seconds. The sensors can be used to detect organic vapors through the intertube electron modulation effect. [Li, 2003] Novak et al used networks of single-walled nanotubes to detect nerve agents. Dimethyl methylphosphonate, a simulant for the nerve agent sarin, was detected in the sub ppb concentration range. Chemical specificity is achieved by the use of filters coated with chemoselective polymer films. Both thin-film transistors and chemiresistor flow cells were fabricated. [Novak, 2003]

RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

There is a need for ESLIs to better serve the user community. Some employers have not implemented satisfactory change-out schedules as required by OSHA. Workers are frequently left on their own to decide when it is appropriate to replace the cartridges and they often do not have the training needed to make an informed decision. While change-out models have made much progress in recent years, many environments are impossible to model adequately, so even diligent employers cannot provide a satisfactory change-out schedule. Colorimetric indicators are slowly being introduced into the respirator cartridge market. Appropriate chemistries have been identified for selected vapors and gases, however, for complex working environments, this technology would be difficult to use because of the specificity of the chemistries. The US military has adopted colorimetric indicators for specific applications. While this is not the ideal sensing technology that they sought, it is an improvement over no indication and meets the unique mission of the warfighter. The US military is very interested in active ESLI and they monitor the progress in the field.

Much preliminary work has been conducted over the past decade on active sensors for ESLI, however, these studies only demonstrated the promising application of ESLIs. There are no in depth studies that provide the details necessary to move ESLI forward. Many questions still need to be answered before ESLI devices are a reality. The ideal sensor has not yet been fully defined. Many issues have been identified, but few challenges have been resolved sufficiently for active sensors to be used as commercial ESLI. All the manufacturers, users, and researchers agree that sensors used for ESLI must be small, cost little and have low power requirements. The sensing technology cannot interfere with the users' performance. Plus viable technologies must be easy to manufacture and maintain. Since different chemicals have different threshold limit values, the sensors must be selective to different chemicals and have sufficient sensitivity to detect the chemicals at their specific exposure limits. These specifications will be difficult to meet, and there are no commercially available sensors that can address all the challenges.

The research efforts in government and industry are important to the overall success of active sensors for ESLI. The three projects that NPPTL is currently addressing are excellent for the advancement of ESLI. The development of the residual life models is important to meeting the needs of the users now. Plus the research is likely to help assess the parameters needed in evaluating ESLI. The work with Cyrano Sciences to develop a small flexible sensor array is also good because it provides a technology to assess specifications such as size, specificity, sensitivity, response time, and sensor location. Finally, the collaboration with Carnegie Mellon University explores cutting edge sensor technologies. Research and development needs to continue. The timing is right due to the interest in sensors for homeland security and the advancements seen in nanotechnology. Much work is necessary before active ESLI become a reality.

Manufacturers have stated that they need the regulations clarified. The performance requirements for ESLI are not clearly defined. NIOSH should have a parallel effort to clarify standards and policy issues. Manufacturers are more likely to pursue ESLI in their product lines if they know how the sensor responses are best used. Operational specifications are needed before manufacturers take the risk of developing ESLI.

It is recommended that the government actively pursue research in active sensors for ESLI. Focused efforts are necessary to advance the state of the art. There are two areas that should be addressed initially, (1) organic vapor respirator cartridges and (2) niche markets. These are suggested because they are likely to have the greatest impact in the near future with an established and/or willing market to support commercialization of new technologies. The two most common gas/vapor substances are paint vapors and solvents, which are present in 41.8% and 32.3% of the establishments that use air-purifying respirators, respectively. Many of the organic vapor cartridges are used by workers employed in "Mom and Pop" shops. This is a high volume market, where the resources are limited for characterizing the workplace environment, therefore change-out policies are sometimes inadequate. In addition, the niche markets are a good place to introduce new technology. Niche markets include: first responders, selected carcinogenic vapors or gases, and other specific chemicals that are not currently acceptable for air-purifying respirators such as hydrazine. Embedded sensors would allow workers to use air-purifying respirators rather than the more costly atmosphere-supplying respirators. It should also be noted that powered air purifying respirators (PAPR) may provide a faster path to commercial implementation since the costs of those devices is significantly higher. Any sensor technologies developed for APR would be directly applicable to PAPR.

Short-Term Research and Development: 3-5 years

There are too many unknown parameters to define the best sensor system at this time. Research is necessary to define some of the design specifications that will be necessary for active sensor systems. It is recommended that commercially available sensors be used to determine some of the operational parameters even if the sensors are not robust enough to meet all the requirements at this time. Incorporation of sensors into cartridges in a realistic manner will expand the knowledge base and help direct future efforts. ESLI will not go forward until several key issues are addressed.

The flexible sensor arrays being investigated by NPPTL are excellent examples of the sensors that should be used in the initial studies for ESLIs. Of the commercially available sensors, chemiresistors are currently the best for this application due to their sensitivity range, small size, and low power requirements. Selectivity is achieved by using arrays of sensors. It is recommended that the application of chemiresistors and other low power sensors such as MIME sensors be pursued first. The efforts should collaborate with cartridge manufacturers to prototype the cartridges with embedded sensors. Studies conducted with prototype systems should be used to define the engineering specifications for the ideal ESLI. Experimental designs are recommended that evaluate sensor design and placement specifications. The projects should address:

Priority 1

- a. How much specificity is required for some typical applications.
- b. The required sensitivity for sensors.
- c. The response time requirements.
- d. The appropriate placement of sensors in the bed or mask.

Priority 2

- e. The appropriate size range for the sensors.

Priority 3

- f. Manufacturing requirements.
- g. User interface preferences.

Priorities 1 and 2 require focused transport studies. Preliminary studies have shown that for well designed filter beds, the wave front for chemicals being transported through the cartridge is uniform and predictable. Experiments are needed that vary the sensor array placement within cartridge beds. The cartridges should then be exposed to well characterized vapors or gases and the output concentrations from the filter bed should be correlated to the sensor responses. The results of these experiments will reveal sensitivity and response time requirements as well as determine proper placement and needed specificity. The efforts should identify specific applications that will be successful in the near term such as organic vapor cartridges for paint vapors and solvents.

Long-Term Research and Development: 3-10 years

There is much interest in sensors for many applications and therefore, opportunities to leverage sensor research for homeland security and medical applications. Research efforts should be focused on the nano-enabled technologies because these sensors have much promise for low power and small size. MIME sensors, MEMS devices, and nanostructured materials look very promising. In addition, research should be directed towards multivariate data analysis and novel signal processing methods. Studies are needed to improve sensor stability, robustness to environmental effects, and to facilitate calibration transfer from sensor to sensor.

Finally, new energy sources may be necessary. Research is underway in areas of production, storage, and exploitation of power for lightweight, long-lived power sources. Some of the many new ideas include: (1) laser-engineered lithium ion microbatteries for next generation microelectronic devices., (2) batteries that harvest energy from micro-

solar cells, (3) high surface area, nanostructured aerogels for higher energy storage capacity, and (4) new nanostructured architectures to achieve higher battery capacity and energy density. Some research efforts should be directed to novel power sources and circuit designs.

An advance in sensors for ESLI requires focused research efforts that examine the entire sensor system/cartridge package. This work is needed because more than 200,000 private establishments use air-purifying respirators according to the NIOSH/BLS <http://www.cdc.gov/niosh/docs/respsurv/> survey of respirator usage among private sector businesses in the United States. In addition, nearly 20% of the establishments reportedly allow their employees to determine when to change their gas/vapor cartridge. Workers at these establishments are at a higher risk of exposure because of potentially inadequate change-out procedures. ESLI devices could potentially reduce exposures for those workers and provide a safer workplace.

APPENDIX A: LITERATURE SURVEY

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APPENDIX B: DISCUSSION PARTICIPANTS

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3M

Survivair

Draeger

Moldex

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APPENDIX C: COMPARISON OF SENSOR TECHNOLOGIES
(provided by Dr. Arthur Snow, Naval Research Laboratory, Code 6123)

| | E-CHEM | MOS | SAW | COND. POLYMER | MIME |
|------------------------------------|-----------------------------------|---|---------------------------------------|-------------------------------|---------------------------------------|
| ANALYTES | LOW MW, ELECTROACTIVE FIXED GASES | COMBUSTIBLES | HIGHER MW, NEUTRAL AND POLAR ORGANICS | ELECTRON DONOR-ACCEPTOR GASES | HIGHER MW, NEUTRAL AND POLAR ORGANICS |
| DETECTION PRINCIPLE | AMPEROMETRIC MEAS. OF REDOX | CONDUCTANCE CHANGE OF HOT SEMICONDUCTOR | MASS CHANGE OF SORBENT FILM | CONDUCTANCE CHANGE OF POLYMER | CONDUCTANCE CHANGE OF NANOCCLUSERS |
| DETECTABILITY | 0.1 PPMV TO 10% | 0.01 PPMV TO 10% | 0.01 PPMV TO 95% | 0.1 PPMV TO 10% | 0.01 PPMV TO 95% |
| SIZE | 5 CC. | <1 CC. | < 0.5 CC | < 0.1 CC | <0.1 CC |
| POWER | <10 mW | < 250 mW | < 100 mW | <10 mW | <10 mW |
| LINEARITY | LINEAR | NON-LINEAR | FAIRLY LINEAR | NON-LINEAR | LINEAR |
| STABILITY | GOOD | FAIR | VERY GOOD | FAIR | VERY GOOD |
| RESPONSE TIME | 1-100 sec | 10-1000 sec | 0.1-100 sec | 10-1000 sec | 0.01- 10 sec |
| SHELF-LIFE | 2 years | 5 years + | 10 years + | 2 years + | LONG |
| MICROSENSOR FIGURE OF MERIT | 5 | 2.5 | 0.5 | 0.1 | 0.01 |